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February 9, 2012

Ms. Demaree Collier
U.S. Environmental Protection Agency
Region 5 (HSRM-6J)
77 West Jackson Blvd.
Chicago, IL 60604

Subject: Request for Approval to Add 1,4-Dioxane to the March 2012 Analytical Program
Lemberger Landfill and Lemberger Transport and Recycling Site
Town of Franklin, Wisconsin

Dear Ms. Collier:

TRC Environmental Corporation (TRC), on behalf of the Lemberger Site Remediation Group (LSRG), has prepared this letter to request approval to modify the March 2012 groundwater analytical program for the Lemberger Site. The proposed program modification is to add 1,4-Dioxane to the analytical list for the March 2012 sampling event as discussed at our January 6, 2012, meeting and January 30, 2012, telephone conversation.

In a letter dated June 1, 2011, the USEPA, in commenting on Revision 1 of the GMP (RMT, April 2011), requested the addition of 1,4-dioxane to the groundwater analytical program at the Lemberger site. The stated rationale for adding 1,4-dioxane to the analytical program is as follows: 1,4-dioxane was used as a stabilizer for 1,1,1-trichloroethane (a compound detected at relatively high concentrations at the site), the regulatory limits for 1,4-dioxane are stringent (PAL = 0.3 µg/L), and recent advances in analytical methodology have resulted in lower attainable detection limits.

In response to this request, TRC proposes the addition of 1,4-dioxane to the groundwater analytical program at the Lemberger site for the March 2012 groundwater monitoring event. The currently approved groundwater monitoring program is summarized in Table 1. The March sampling event represents the semi-annual monitoring program, and includes the sentinel wells, the near-field wells, the deep wells, and 23 residential wells. In addition, nine of the 28 plume wells are sampled during the semi-annual event. The coverage area provided by the semi-annual sampling event will be adequate to determine the presence and extent of 1,4-dioxane within the groundwater plume area.

Pace Analytical Laboratories (Pace), the USEPA approved laboratory for the Lemberger site, does not currently have the capability to detect 1,4-dioxane down to the PAL

(0.3 µg/L). In order to reach the required detection limits, TRC proposes that the water samples for the 1,4-dioxane analysis are sent to the Test America (TA) Laboratory located in Burlington, Vermont. The TA laboratory runs water samples for 1,4-dioxane by Gas Chromatography/Mass Spectrometry (GC/MS) with Selected Ion Monitoring (SIM) (Method 522 Modified), and can achieve an Limit of Detection (LOD) of 0.067 µg/L, and Limit of Quantitation (LOQ) of 0.2 µg/L. The laboratory SOP for this analysis is attached for your review. The TA Burlington laboratory is not certified in the State of Wisconsin; however, this laboratory holds National Environmental Laboratory Accreditation Program (NELAP) certification.

TRC, on behalf of the LSRG, is requesting approval of the one-time program modification described above, and the use of the TA Burlington laboratory for the 1,4-dioxane analysis for the March 2012 sampling event. Once the data are received and validated, the results of the 1,4-dioxane analyses will be evaluated, summarized in a letter report, and recommendations for future monitoring will be made.

If you have any questions regarding the proposed modifications, please call me at 608-826-3637.

Sincerely,

TRC Environmental Corporation

Kristopher D. Krause, P.E.
Senior Project Manager

Attachments

cc: Mr. Gary Edelstein – Wisconsin DNR
Ms. Annette Weissbach – Wisconsin DNR
Mr. Doug Clark – Foley & Lardner
Mr. Nilaksh Kothari – Manitowoc Public Utilities
Mr. James Wallner – Red Arrow Products Co., Inc.
Mr. Louis Meschede – Newell Rubbermaid
Ms. Juliana Ruenzel – City of Manitowoc
Mr. Tim Reis – The Manitowoc Company, Inc.
Mr. John Lang – Quantum Management Group, Inc.

Table 1
Current Long-Term MNA Sampling Program
Lemberger Sites Monitoring Plan

WELL GROUPING/ DESIGNATIONS	SAMPLING FREQUENCY	LABORATORY ANALYTICAL PARAMETERS[1]	FIELD ANALYTICAL PARAMETERS[1]
Monitoring Wells: RM-001D, RM-001I, RM-002D, RM-002I, RM-003D, RM-003I, RM-004D, RM-004S, RM-005D, RM-005I, RM-005S, RM-007D, RM-007S, RM-007XD, RM-007XXD, RM008D, RM-010D, RM-011D, RM-101D, RM-101I, RM-102D, RM-103D, RM-103S, RM-201D, RM-201I, RM-202D, RM-202I, RM-203D, RM-203I, RM-204I, RM-204D, RM-205D, RM-205I, RM-206S, RM-207S, RM-208XD, RM-208D, RM-208I, RM-208S, RM-209D, RM-210D, RM-210I, RM-211D, RM-212D, RM-212I, RM-213D, RM-214D, RM-301S, RM-302S, RM-303D, RM-304D, RM-305D, RM-306D, RM-307D, RM-308D	Quarterly (March, June, September and December)	None	Depth to Water
Extraction Wells: EW-01D, EW-02D, EW-03D, EW-04D, EW-04I, EW-06D, EW-06S, EW-07D, EW-08D, EW-09D	Quarterly (March, June, September and December)	None	Depth to Water
Observation Wells: OW-101A, OW-101B, OW-102A, OW-102B, OW-102C, OW-102D, OW-103A, OW-103B, OW-104A, OW-104B, OW-104C, OW-104D, OW-104E, OW-104F, OW-104G, OW-104H, OW-105A, OW-105B, OW-106A, OW-106B	Quarterly (March, June, September and December)	None	Depth to Water

Table 1 (continued)
Current Long-Term MNA Sampling Program
Lemberger Sites Monitoring Plan

WELL GROUPING/ DESIGNATIONS	SAMPLING FREQUENCY	LABORATORY ANALYTICAL PARAMETERS[1]	FIELD ANALYTICAL PARAMETERS[1]
Leachate Head Wells: LH-01, LH-02B, LH-03, LH-04, LH-05, LH-06, LH-07, MW-14R, MW-15R	Quarterly (March, June, September and December)	None	Depth to Water
Leachate Extraction Wells: LW-01, LW-02, LW-03, LW-04, LW-05, LW-06, LW-07, LW-08	Quarterly (March, June, September and December)	None	Depth to Water
Sumps: GWC-1, GWC-2, GWC-3	Quarterly (March, June, September and December)	None	Depth to Water
LTR Sentinel Wells: RM-3D[2], RM-211D, RM-212I, RM-212D, RM-2D, RM-210I, RM-210D, RM-203I, RM-203D	Quarterly (March, June, September and December)	VOCs	pH, temperature, specific conductance, ORP, turbidity, DO
LTR Near-Field Wells: RM-303D, RM-209D, RM-5D, RM-7S, RM-7D, RM-7XD, RM-8D, RM-208D, RM-214D	Quarterly (March, June, September and December)	VOCs	pH, temperature, specific conductance, ORP, turbidity, DO
LTR Deep Wells: RM-7XXD, RM-208XD	Quarterly (March, June, September and December)	VOCs (incl. methane, ethane, & ethene) alkalinity, manganese, nitrate+nitrite, sulfate, and TIC	CO_2, pH, temperature, specific conductance, ORP, turbidity, DO
LTR Plume Wells[3]: RM-101D, RM-103D, RM-204I, RM-204D, RM-213D, RM-304D, RM-305D, RM-306D, RM-307D	Semi-annually (March, September)	VOCs	pH, temperature, specific conductance, ORP, turbidity, DO

Table 1 (continued)
Current Long-Term MNA Sampling Program
Lemberger Sites Monitoring Plan

WELL GROUPING/ DESIGNATIONS	SAMPLING FREQUENCY	LABORATORY ANALYTICAL PARAMETERS[1]	FIELD ANALYTICAL PARAMETERS[1]
LTR Plume Wells: RM-2I, RM-3I, RM-4S, RM-4D, RM-5I, RM-10D, RM-11D, RM-101I, RM-102D, RM-103S, RM-201I, RM-201D RM-202I, RM-202D RM-205I, RM-205D, RM-208S, RM-208I, RM-308D	Annually (September)	VOCs	pH, temperature, specific conductance, ORP, turbidity, DO
LL Wells[4]: RM-5S, RM-207S, RM-206S, RM-301S, RM-302S	Annually (September)	VOCs	pH, temperature, specific conductance, ORP, turbidity, DO
Residential Wells: GR-8, GR-9, GR-10, GR-11, GR-12, GR-13, GR-14, GR-15, GR-16, GR-17, GR-24, GR-25, GR-26, GR-27, GR-30, GR-31, GR-33, GR-41, GR-60R, GR-62, GR-63, GR-64, GR-65	Semi-annually (March, September)	VOCs	pH, temperature, specific conductance, ORP, turbidity, DO

Notes:
[1] = MNA laboratory and field-analytical methods and reporting limits are listed in Table 3 of the MNA Summary Report.
[2] = RM-3D moved from annual to quarterly sampling, per USEPA request.
[3] = This list of LTR plume wells moved from annual to semi-annual, per WDNR request.
[4] = RM-301S, RM-302S and RM-5S are located inside of the LL slurry wall.

VOCs = Volatile organic compounds, laboratory analyzed via EPA Method 8260B.
TIC = Total Inorganic Carbon.
CO_2 = Carbon dioxide.
ORP = Oxidation-reduction potential.
DO = Dissolved oxygen.

Title: 1,4-Dioxane in Water by GC/MS/SIM (Method 522 MOD)

Approval Signatures:

William S. Cicero
Laboratory Director

Kristine A. Dusablon
Department Manager

Kirstin L. McCracken
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Technical Director

Daniel W. Helfrich
Health & Safety Coordinator

Approval Date: May 20, 2011

Facility Distribution No. Electronic **Distributed To: Facility Intranet**

The controlled copy of this SOP is the PDF copy of the SOP that is posted to the laboratory's SOP Directory. Printed copies of this SOP or electronic copies of this SOP distributed outside the facility are considered uncontrolled.

1.0 Scope and Application

This standard operating procedure (SOP) describes the laboratory's analytical procedure used to determine the concentration of 1,4-Dioxane in extracts created by the preparation of water samples extracted using SPE (solid phase extraction).

This SOP includes procedures for extraction and analysis.

1.1 Analytes, Matrix(s), and Reporting Limits

This procedure may be used for surface and groundwater samples.

The list of target compounds that can be determined from this method along with the associated reporting limit (RL) is provided in Table 1.

2.0 Summary of Method

Following solvent extraction 2 uL of extract is injected onto a GC system which uses a temperature program to separate the target compounds which are then detected by a mass spectrometer (MS). The target analytes are identified by comparison of their mass spectra with the electron impact (or electron impact-like) spectra of standards acquired using the same operational parameters. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

This procedure is based on the following reference method:

- Method 522 Determination of 1,4-Dioxane in Drinking Water By Solid Phase Extraction (SPE) and Gas Chromatography/Mass Spectrometry (GC/MS) With Selected Ion Monitoring (SIM), Version 1, September 2008.

If the laboratory's procedure is modified from the reference method, a list of these modifications can be found in Section 16.0 of this SOP.

3.0 Definitions

A list of terms and definitions are provided in Appendix A.

4.0 Interferences

- Contaminants in solvents, reagents, glassware, and other sample processing hardware may cause method interferences such as discrete artifacts and/or elevated baselines in the extracted ion current profiles (EICPs). All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source.

- Injection syringes should be adequately flushed with solvent between injections in order to remove all traces of the prior sample.

- Contamination by carryover is possible whenever high and low concentration samples are analyzed in sequence. Samples are screened prior to analysis so that the proper dilution analysis is performed. Re-analysis is performed if carryover is suspected.

- Co-extracted Interferences may include lipids, polymers, copolymers, proteins, natural resins, cellular components, viruses, steroids, and high-molecular weight compounds. GPC, which is size exclusion chromatography, is appropriate for cleanup of these types of polar and non-polar interferences.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

Latex and vinyl gloves provide no protection against the organic solvents used in this method. Nitrile or similar gloves must be used.

The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2 Primary Materials Used

Table 2 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

6.1 Miscellaneous

- 2 mL Autosampler vials with 200 uL inserts, PFTE crimp top, National Scientific or equivalent.
- 4 mL sample vials with PFTE lined screw top caps, National Scientific or equivalent
- Volumetric Syringes, Class "A", Assorted sizes, Hamilton or equivalent.
- SPE Vacuum box
- Conical collection tubes with graduations
- Supleco ENVI-Carb Plus SPE cartridges cat#54812-U

6.2 Computer Hardware/Software

- GCMS Acquisition Platform - Hewlett-Packard ChemStation.
- Data Processing - Hewlett-Packard 9000-series computers, HP 9000 K200 (Chemsvr6)/ HP-UX 10.20 and Target V3.5.

6.3 Instrumentation

- SVOA Autosampler: HP7673A™, CTC A200S™ or equivalent.
- Gas Chromatograph: Hewlett-Packard™ 5890 GC, 6890 GC or equivalent.
- Mass Spectrometer: Hewlett-Packard™ 5971 MSD, 5972 MSD, 5973 MSD and 5975 MSD or equivalent.
- Primary Column, Crossbonded, 5% diphenyl – 95% dimethyl polysiloxane, 30 m x 0.25 mmID x 0.50 um film thickness: Restek™ RXi-5ms or equivalent.
- Guard Column: Restek™ Deactivated 5m x 0.25 mm ID or equivalent.
- Column unions: Restek Press-Tights™ or equivalent.
- Injection port liners: Single Goose Neck, borosilicate glass. Restek™ 20799 or equivalent.
- Injection Port Septa: HP™, 11 mm Thermo Red or equivalent.
- Data System: Hewlett-Packard Chem server™, Target 3.5 processing software and Hewlett-Packard ChemStation software for instrument control and acquisition

7.0 Reagents and Standards

7.1 Reagents

- Acetone: Pesticide Residue Analysis Grade, JT Baker or equivalent.
- Methylene Chloride (CH_2Cl_2): Pesticide Quality, J.T. Baker or equivalent.
- Methanol (MeOH): Pesticide Quality, J.T. Baker or equivalent.
- Hexane (CH_3 $(CH_2)_4CH_3$): Pesticide Quality, J.T. Baker or equivalent.
- Toluene ($C_6H_5CH_3$): Pesticide Quality, J.T. Baker or equivalent.
- Sodium Sulfate (granular, anhydrous), Na_2SO_4. J.T. Baker or equivalent. Purify by heating at 400°C for at least 4 hours.

7.2 Standards

Purchase stock standard solutions from commercial vendors. Prepare calibration and working standards by diluting a known volume of the purchased stock standard in an appropriate solvent to the final volume needed to achieve the desired concentration. The recommended formulation for each standard used in this procedure is provided in Appendix B along with the recommended source materials, expiration dates and storage conditions.

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection so these procedures are not included in this SOP. Sampling requirements may be found in the published reference method.

Listed below are the recommended sample size, preservation and holding time requirements:

Matrix	Sample Container	Routine Sample Size	Preservation	Holding Time	Reference
Water	Amber glass bottle	1 Liter	pH<2 and Chilled to <4°C	Extraction: 28 days Analytical: 28 days	Method 522 Sec. 8.4

Extraction holding time is determined from sampling date; analytical holding time is determined from date of initiation of extraction.

Unless otherwise specified by client or regulatory program, after analysis, samples and extracts are retained for a minimum of 30 days after provision of the project report and then disposed of in accordance with applicable regulations.

9.0 Quality Control

9.1 Sample QC

The laboratory prepares the following quality control samples with each batch of samples.

QC Item	Frequency	Acceptance Criteria
Method Blank (LRB)	1 in 20 or fewer samples	See Table 3
Laboratory Control Sample (LFB)	1 in 20 or fewer samples	See Table 3
Matrix Spike(s) FLSM	1 in 20 or fewer samples	See Table 3
Sample Duplicate (FD or FLSMD)	1 in 20 or fewer samples	See Table 3

Surrogate spikes are added to all field and QC samples before preparation and/or analysis to assess the effect of the sample matrix on the accuracy of the method in the specific sample matrix.

Internal standards are added to all field and QC samples prior to analysis.

9.2 Instrument QC

The following instrument QC is performed:

QC Item	Frequency	Acceptance Criteria
BFB	Prior to initial calibration	See Table 3
Initial Calibration (ICAL)	Initially, when ICV or CCV indicate linearity is no longer	See Table 3

	valid	
Second Source Calibration Verification (ICV)	Once, after each ICAL	See Section Table 3
Continuing Calibration Verification (CCV)	Daily at the beginning and end of each analytical sequence and after every ten field samples	See Section Table 3

10.0 Procedure

10.1 Sample Preparation

Allow samples to come to room temperature prior to extraction. Spike each 100 mL sample, blank, and QC sample aliquot with 100 uL of the 2 ug/mL surrogate solution. Spike each 100 mL QC sample aliquot with 100 uL of the 2 ug/mL LCS/Matrix spike solution (mid level LFB). Set-up the solid phase cartridge vacuum box with a sufficient number of ENVI-Carb Plus SPE cartridges for the number of samples in the batch plus one for the procedural blank and one for the LCS.

Condition each cartridge using the following procedure: Add 1 mL of MeCl and aspirate completely using vacuum. Place a reservoir over each cartridge, fill with approximately 2 mL of methanol and aspirate completely using vacuum. Fill each cartridge with approximately 2 mL of methanol and elute with vacuum until the methanol level is at the top of the sorbent. DO NOT allow the cartridge to go dry. Fill the cartridge with 3 mL of reagent water and elute under vacuum until the water level is at the top of the sorbent without letting the cartridge go dry.
Extract each sample, blank, and QC sample with the following procedure: Fill reservoir with sample. Adjust vacuum so that the approximate flow rate is 10 mL/min. Elute 100 mL of each sample. After all of the sample has passed through the cartridge draw air through the cartridge for 10 min at full vacuum.

Elute each sample into a conical collection tube placed below the cartridge using the following procedure: Add 2 mL of MeCl to each cartridge and allow the MeCl to soak the sorbent for 1 min without vacuum. Apply low vacuum and collect the MeCl from the cartridge, dropwise, into the conical collection tubes. Continue to add small amounts of MeCl until approximately 1.5-2.0 mL of solvent have been collected in the conical tubes. Remove the tubes, adjust the volumes to 2 mL with MeCl. Add approximately 1 g of Na2SO4 and vortex gently to dry the extract. Transfer the remaining extract to a 2 mL amber extract vial and seal with a PFTE lined screw cap. Deliver extracts to instrumental laboratory for analysis.

10.2 Instrument Operating Conditions

Gas Chromatography/Mass Spectrometry – Set the instrument to acquire and store analytical data using the SIM parameters detailed below with a total cycle time (including scan overhead time) of one second per scan or less and at 70 electron volts. Adjust the cycle time to measure five or more spectra during the elution of each GC peak.

Solvent Delay: 2.20 min
EM Offset: 200
Ions : Dwell time (ms)

57: 50	58: 50	88:50
96:50	64:50	

46:50 78:50 80:50

A typical GC temperature program used by the laboratory is as follows:

Initial Temperature:	40°C for 0.5 minutes.
Temperature Program:	10°C/min to 80°C for 0 min. then 100°C/min to 250°C for 0 min.
Injector Temperature:	220°C
Transfer Line Temperature:	300°C
Injector:	Grob-like, splitless
Injection volume:	2 µL
Carrier Gas:	Helium

10.3 Tune Standard (BFB)

To initiate the analytical sequence inject a 2 µL aliquot of BFB (2 µg/mL) into the GC. The data processing system acquires and averages three scans (apex scan, scan prior, and scan following) and performs background subtraction of the single scan prior to the elution of the BFB. The results of the BFB must meet the tune criteria given in Table 4 before instrument calibration can proceed. If criteria are not met, retune the instrument.

10.4 Instrument Calibration

10.4.1 Initial Calibration (ICAL)

Calibrate the instrument with a minimum of five calibration standards for each target analyte at concentrations that span the working range of the method. Analyze ICAL standards at the recommended concentrations of 0.002, 0.020, 0.100, 0.200, 0.400 ng/uL.

Prepare each calibration standards in an autosampler vial using the formulations found in Appendix B. The final internal standard concentration in extract will be 0.50 ng/uL.

Inject 2 uL of each standard onto the instrument system.

The following criteria should be met for a calibration to be considered acceptable. If criteria are not met, perform corrective action prior to further analysis. Recommended corrective actions are provided in Table 3.

- The mean (or minimum) RF for the target analyte and surrogate should be greater than 0.050.
- The Relative Retention Time (RRT) for each target analyte in each calibration standard should agree within 0.06 RRT units.
- When quantitated using the calibration curve, each calibration point, except the lowest point, should calculate to be within 80-120% of its true value. The lowest point should calculate to be within 60-140% of its true value. If these criteria cannot be met, the analyst will have difficulty meeting ongoing QC criteria. It is recommended that corrective action be taken to re-analyze the CALs, restrict the range of calibration, or select an alternate method of calibration.

Alternate Quantification Option:

Linear Regression & Weighted Linear Regression: Generate a curve of concentration vs. response for each analyte and calculate the correlation coefficient. The calibration must have a correlation coefficient (r) $\geq$ 0.99. If this criterion is not met, correct the problem and repeat the calibration. The use of linear regression requires a minimum of 5 calibration points.

10.4.2 Second Source Calibration Verification (ICV)

Verify the calibration with a second source standard. The second source standard must be prepared from a different manufacturer than the calibration standards unless only one manufacturer exists, in which case, the second source standard must be from a different lot than the lot used for the calibration standards.

Prepare the ICV solution (0.200 ng/uL) using the formulations provided in found in Appendix B. Add internal standard and inject 2 uL of the ICV onto the instrument system. Acquire the data and evaluate the results.

The percent recovery of the ICV must be ±20% of the expected value for each analyte. If this criterion is not met, correct the problem and reanalyze the ICV. If the reanalysis fails, perform corrective action and if necessary remake the standards and recalibrate.

10.4.3 Continuing Calibration Verification (CCV)

Analyze a continuing calibration verification standard (CCV) daily at the beginning and end of each analytical sequence and after every ten field samples. The concentration of the initial daily CCV should be at or near the low calibration level standard (and/or MRL). Subsequent CCVs may alternate between the mid and high level calibration concentrations.

Inject 2 uL of the prepared CCV standard, acquire the data and evaluate the results.

The following criteria must be met:

The calculated amount in the initial low level CCV must within ±50% of the true value, calculated amounts for the mid or high level CCVs must be within ±30%.

The internal standard retention time should be evaluated immediately after or during data acquisition. If the retention of the internal standard exceeds the 0.06RRT units from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required. Retention time shifts that are the result of routine column maintenance (clipping the column) are evaluated and may be considered acceptable.

The extracted ion current profile (EICP) area of the internal standard in the calibration verification standard should not change by more than ±30% from the most recent CCV. If the EICP area for any of the internal standard in the calibration verification standard changes, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

If the CCV fails, it may be repeated once. If repeat analysis fails, corrective action must be taken.

- If the CCV is biased high and there are no detects for the failing analytes in the sample, the non-detects may be reported against the failing CCV.

- If the CCV is biased low and the sample results for the failing analytes exceed a maximum regulatory limit or action level, the sample results may be reported against the failing CCV.

Any sample result associated with a CCV failure must be qualified with an explanation provided in the case narrative.

Troubleshooting:

Check the following items in case of calibration failures:

- Loss of sensitivity for higher boiling compounds and internal standards may be indicative of a leak at the inlet. Replace septa and/or re-tighten lower inlet connection.
- Carryover contamination may indicate empty rinse vials.

10.5 Screen Procedure

At the discretion of the laboratory, sample extracts may be screened prior to analysis with a GC-FID or a GC/MS system.

10.6 Analysis

Remove the extracts from storage and let them warm to room temperature. Transfer 100 uL of extract to a 1 mL auto-sampler vial with insert. Add 4 uL of the internal standard solution to each vial and seal the vial with a PTFE lined crimp top cap. If a different extract volume is used (e.g. 50 uL), adjust the internal standard volume proportionately (2 uL of IS).

If the extract was screened and the screen results indicate a primary dilution is required, dilute the extract in methylene chloride. If the relative volumes needed for a single dilution step exceed the accuracy of the syringes, perform serial dilutions. For example, if a sample requires a 0.1% analysis in order to have target constituents within the upper half of the calibrated range, 0.1 uL of a 100 uL extract aliquot is needed to perform the dilution but the gradations of the syringe are to 0.2 uL. In this instances, perform a serial dilution of 1:100 (1.0%) and 10:100 (10%) to achieve an analysis concentration of 0.1%.

Arrange the samples in a sequence that begins with the calibration standards followed by the analysis of QC samples, field samples, and continuing calibration verification standards (CCVs).

An example analytical sequence for our routine compound list that includes initial calibration (ICAL) is provided below.

Injection Number	Lab Description
1	BFB Tune Standard
2	ICAL 5 (0.400 ng/uL)
3	ICAL 4 (0.200 ng/uL)
4	ICAL 3 (0.100 ng/uL)

5	ICAL 2 (0.020 ng/uL)
6	ICAL 1 (0.002 ng/uL)
7	ICV (0.200 ng/uL ICV)
"	CCV 3 (0.002 ng/uL)
"	Up to 10 field samples
"	CCV (0.100 ng/uL)
"	Up to 10 field samples
"	CCV (0.400 ng/uL)
"	Continue until a new calibration is needed.

Enter the sample ID's into the data acquisition program in the order the samples were placed in the autosampler and initiate the analytical sequence.

11.0 Calculations / Data Reduction

11.1 Qualitative Identification

The data system tentatively identifies target analytes by comparing the retention time of the peaks to a window set around the daily calibration standard, and searches in that area for the primary and up to two secondary ions characteristic of the target analyte. Tentative identifications made by the computer are reviewed and either accepted or rejected by the analyst using the following criteria:

- NOTE: This method uses an MSD operating in SIM mode. Identification of target analytes is made by comparison of its background subtracted mass spectrum to a reference spectrum in the user-created database. Particular attention should be directed at the peak ions relative intensity versus localized background. A sufficient response may be one that exhibits a signal to noise ratio of 3-to-1 or better. In general, all monitored ions should be present at a signal to noise greater than 3-to-1 and their EICP peak maxima agree.

- The GC retention time for the target analyte should be within 0.06 RRT units of the daily standard.

Identification is hindered when components are not chromatographically resolved from interfering analyte peaks or non-target constituents (background). When chromatographic peaks obviously indicate contribution from more than one component (broadened peak with shoulder(s) or a valley between two or more maxima), examine the EICPs to select the appropriate analyte spectra over the entire peak and use selective background subtraction in order to positively identify target analytes and account for extraneous ions. For coeluting compounds, the identification criteria will be met, but the analyte spectrum will contain extraneous ions contributed by the coeluting compound.

Complex environmental matrices, baseline upsets, coelution and peak shape variation can complicate automatic data system integration causing inaccurate and/or missed identification that should be corrected with manual integration. To assure accurate qualitative identification, optimize the data system integration parameters to ensure consistency in integration between standards and sample and evaluate each chromatogram to verify the identification for each target analyte.

11.1.1 Tentatively Identified Compounds (TICs)

Due to the utilization of SIM mode sample acquisition, TIC reporting is not feasible by this method.

11.2 Quantitative Identification

The data system quantifies the concentration of the target compound based on the integrated abundance of the characteristic ion from the EICP using the equations given in Appendix C. If there is matrix interference with the primary ion, a secondary ion may be used for quantification by calculating a mean RF factor for that ion and using that ion to quantify the analyte in the sample. When secondary ion calculations are performed, initiate a nonconformance memo (NCM) to ensure the quantitation approach is reported in the project narrative.

11.3 Calculations

See Appendix C.

11.4 Data Review

11.4.1 Primary Review

Review project documents to ensure those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Confirm qualitative and quantitative identification criteria using the criteria provided in Sections 11.1 and 11.2. If the data system does not properly integrate the peaks perform and document manual integration in accordance with laboratory SOP BR-QA-006.

Upload the data files from the data processing system to the laboratory information management system (TALS). Complete the batch information for standards and reagents and verify ICAL and QC sample associations. Review the results and set results to primary, secondary, acceptable or rejected as appropriate. Dilute and reanalyze samples whose results exceed the calibration range. The dilution analysis should result in a determination within the calibration range, preferably in the upper half of the calibration range. A more concentrated analysis is not necessary unless the project requires it. Dilution analyses may be performed to minimize matrix interference.

If a sample was analyzed immediately following a high concentration sample, review the results of the sample for any sign of carryover. If carryover is suspected, reanalyze the sample.

Create a non-conformance report (NCM) for any calibration, QC and sample data that is reported outside established acceptance criteria and/or schedule necessary corrective action. Set batch to 1st level review and complete the data review checklist.

The following analytes have been identified as poor performing analytes in some matrices based on statistical data. Consequently corrective action will not be taken when LCS or MS/MSD recovery is not within established limits for these analytes. Initiate a NCM to document the exceedance and indicate poor performing analyte as the justification for not taking corrective action.

11.4.2 Secondary Data Review

Verify quantitative and qualitative identification in the initial calibration standards and spot check ~15% of the remaining data in the batch.

If manual integrations were performed:

- Review each integration to verify that the integration meets the requirements for manual integration as specified in laboratory SOP BR-QA-006. If an error is suspected or found consult with the analyst that performed the integration analyst and request correction or notify the Department Manager, Technical Director or QA Manager. Do not "fix" the integration. Reintegration by a secondary data reviewer must not be performed except in limited circumstances as approved by the department supervisor or other laboratory management. If those instances where the secondary reviewer performs the integration, this person is now considered the primary analyst and each integration performed by the secondary reviewer must be subsequently reviewed by a peer analyst or the department supervisor to verify the integration is consistent and compliant with the requirements specified in laboratory SOP BR-QA-006.

- Check to ensure an appropriate technical reason code is provided for each manual integration. Acceptable technical reason codes are provided in laboratory SOP BR-QA-005.

Review project documents to ensure those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Verify that the acceptance criteria for the calibration and QC items listed in Table 1 were met. If the results do not fall within the established limits verify the recommended corrective actions were performed. If not, initiate corrective actions and/or verify an NCM was created to document the criteria exception. Verify analytical results are qualified accordingly. Set batch to 2nd level review and complete the data review checklist.

11.5 Data Reporting

The report format, application of data qualifiers and creation of the data deliverable is performed by the LIMS using the formatter set by the project manager during log-in.

Records of electronic and hardcopy data are maintained as described in laboratory SOP BR-QA-014.

12.0 Method Performance

12.1 Limit of Detection (LOD) and Limit of Quantitation

Establish a LOD and LOQ at initial method set up following the procedures specified in Method 522. The frequency of LOD and LOQ verification depends on the strictest frequency of the regulatory program for which the method supports. The frequency requirement is documented in a spreadsheet maintained by the QA Department.

12.2 Demonstration of Capabilities (DOC)

Perform a method demonstration of capability at initial set-up and when time there is a significant change in instrumentation or procedure.

Each analyst that performs the analytical procedure must complete an initial demonstration of capability (IDOC) prior to independent analysis of client samples. Each analyst must demonstrate on-going proficiency (ODOC) annually thereafter. DOC procedures are further described in the laboratory's quality system manual (QAM) and in the laboratory SOP BR-QA-011.

12.3 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

Instrument analysts, prior to independent analysis of client samples, must also have documentation of demonstration of initial proficiency (IDOC) and annual on-going proficiency (ODOC) in their employee training files.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001 *Hazardous Waste*. The following waste streams are produced when this method is carried out.

- Vials containing sample extracts - Satellite Container: 30 gallon waste drum
- Methylene Chloride solvent waste - Satellite Container: 40mL vials and 4L bottle.

15.0 References / Cross-References

- Method 522 Determination of 1,4-Dioxane in Drinking Water By Solid Phase Extraction (SPE) and Gas Chromatography/Mass Spectrometry (GC/MS) With Selected Ion Monitoring (SIM), Version 1, September 2008. .
- Laboratory SOP BR-QA-005
- Laboratory SOP BR-QA-011
- Laboratory SOP BR-EH-001
- Laboratory SOP BR-QA-014
- Laboratory SOP BR-QA-006 Manual Integration Requirements
- Laboratory Quality Assurance Manual (QAM)
- DoD QSM

16.0 Method Modifications

Modification Number	Method Reference	Modification
1	Method 522 Sec. 1.1	The laboratory performs the method on ground and surface waters only. Drinking water sample preservation requirements are not applied.
2	Method 522 Sec. 7.2	The laboratory does not store standards at <0 °C. All standards are stored at the recommendations of the manufacturer prior to initial use and then at 4 °C once prepared.
3	Method 522 Sec. 8.4	The laboratory stores sample extracts at 4 °C
4	Method 522 Sec. 10.2.2.1	The laboratory utilizes a 2 uL injection volume for all standards, QC and field samples.
5	Method 522 Sec. 10.2.3	The laboratory uses average RFs to establish the calibration curve versus a linear or quadratic model.

17.0 Attachments

- Table 1: Routine Target Analyte List & Reporting Limits (RL)
- Table 2: Primary Materials Used
- Table 3: QC Summary, Frequency, Acceptance Criteria and Recommended Corrective Action
- Table 4: BFB Key Ions and Abundance Criteria
- Table 5: Control Limits for Accuracy (%R) and Precision (RPD)
- Appendix A: Terms and Definitions
- Appendix B: Standard Preparation Tables
- Appendix C: Equations

18.0 Revision History

BR-MS-, Revision 0:

Table 1: Target Analyte List & Reporting Limits (RL)

Compound	CAS	Compound Type	ISTD Group	RL ug/L	Quant mz	Qual mz	Qual mz
1,4-Dioxane	319-84-6	TARGET	1	0.20	88	58	57
Tetrahydronfuran-d8		ISTD	1		46	80	78
1,4-Dioxane-d8	877-09-8	SSTD	1		96	64	

Table 2: Primary Materials Used

Material[1]	Hazards	Exposure Limit[2]	Signs and Symptoms of Exposure
Toluene	Flammable Poison Irritant	200 ppm-TWA 300 ppm-Ceiling	Inhalation may cause irritation of the upper respiratory tract. Symptoms of overexposure may include fatigue, confusion, headache, dizziness and drowsiness. Peculiar skin sensations (e. g. pins and needles) or numbness may be produced. Causes severe eye and skin irritation with redness and pain. May be absorbed through the skin.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.

[1] Always add acid to water to prevent violent reactions.
[2] Exposure limit refers to the OSHA regulatory exposure limit.

Table 3: QC Summary, Frequency, Acceptance Criteria and Recommended Corrective Action

QC	Minimum Frequency	Acceptance Criteria	Recommended Corrective Action[1]
Tune Standard	Prior to initial calibration	See Table 4	Reanalyze, retune mass spectrometer; no samples may be analyzed without a valid tune.
ICAL	Before sample analysis, when CCVs indicate calibration is no longer valid; after major instrument maintenance	From the calibration curve each calibration level must back calculate to within ±20%, ±40% for the low cal level.	Correct problem then repeat calibration, no samples may be analyzed until criteria are met.
ICV	With each initial calibration	% Recovery within ±20% of expected value	Correct problem and verify second source standard. Reanalyze. If that fails, repeat initial calibration; no samples should be analyzed without an acceptable ICV.
CCV	Daily at the beginning of each analytical sequence, every 10th field sample and at the end of the sequence at alternating concentrations	Low level ±50% Mid level ±30% High level ±30%	Re-analyze once, if still outside criteria perform corrective action repeated failures require new ICAL and all associated samples since last successful CCV, unless CCV is high and samples are non-detects.
MB (LRB)	One per extraction batch of 20 or fewer samples	Routine: < 1/3 RL	Examine project DQO's and take appropriate corrective action, which may include re-analysis of MB, re-extraction of batch, and/or non-conformance report (NCR). Corrective action must be documented on NCR. If there are no detects in samples, or if all detects are > 10 X MB level, re-prep and reanalysis may not be required.
LCS (LFB)	One per extraction batch of 20 or fewer samples	See Table 5 & Section 13.1.1 (ME)	Examine project DQO's and take appropriate corrective action, which may include re-analysis of LCS, re-extraction of batch, and/or non-conformance report (NCR). Corrective action must be documented on NCR. Flag all reported values outside of control limits.
MS/MSD (FLSM/FLSMD)	One per extraction batch of 20 or less samples.	See Table 5 & Section 13.1.1 (ME)	Evaluate data and determine if a matrix effect or analytical error is indicated. If analytical error, re-analyze and/or re-extract. Flag all reported values outside of control limits.
Surrogate Standard	All field and QC samples	See Table 5	Evaluate data and determine if a matrix effect or analytical error is indicated. If analytical error, re-analyze or re-extract. If matrix effect, review project DQOs to determine if a matrix effect must be confirmed by re-analysis. Flag all reported values outside of control limits.
Internal Standard	All field and QC samples	EICP area ±30% of that in the most recent CCV. RT ± 30 seconds from RT of midpoint of ICAL.	Inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

[1] *The recommended corrective action may include some or all of the items listed in this column. The corrective action taken may be dependent on project data quality objectives and/or analyst judgment but must be sufficient to ensure that data quality is known and documented. If corrective action is not taken or is not successful, data must be flagged with appropriate qualifiers.*

Table 4: BFB Key Ions and Abundance Criteria

m/e	ION ABUNDANCE CRITERIA
95	Base Peak, 100% relative abundance
50	15.00 - 40.00% of mass 95
75	30.00 - 80.00% of mass 95
96	5.00 - 9.00% of mass 95
173	Less than 2.00% of mass 174
174	50.00 - 120.00% of mass 95
175	5.00 - 9.00% of mass 174
176	95.00 - 101.00% of mass 174
177	5.00 - 9.00% of mass 176

Table 5: Control Limits for Accuracy (%R) and Precision (RPD)

Compound	Lower % Recovery	Upper % Recovery	RPD %
1,4-Dioxane (RL LFB)	50	150	
1,4-Dioxane (Mid – high LFB)	70	130	
1,4-Dioxane (FLSM/D)	70	130	30
Surrogate			
1,4-Dioxane-d8	70	130	

Appendix A: Terms and Definitions

Acceptance Criteria: specified limits placed on characteristics of an item, process or service defined in requirement documents.

Accuracy: the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

Analyte: The specific chemicals or components for which a sample is analyzed. (EPA Risk Assessment Guide for Superfund, OSHA Glossary).

Batch: environmental samples that are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria. An analytical batch is composed of prepared environmental samples (extracts, digestates and concentrates), which are analyzed together as a group.

Calibration: a set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, or values represented by a material measure or a reference material and the corresponding values realized by the standards.

Calibration Curve: the graphical relationship between the known values or a series of calibration standards and their instrument response.

Calibration Standard: A substance or reference used to calibrate an instrument.

Calibration Check Compounds (CCCs): Selective analytes from the compound list that are used to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

Corrective Action: the action taken to eliminate the cause of an existing nonconformity, defect or other undesirable occurrence in order to prevent recurrence.

Data Qualifier: a letter designation or symbol appended to an analytical result used to convey information to the data user. (Laboratory)

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Internal Standard: a known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS, LFB): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix Spike (MS, FLSM): a field sample to which a known amount of target analyte(s) is added.

Matrix Spike Duplicate (MSD, FLSMD): a second replicate matrix spike

Method Blank (MB, LRB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are not produced in this range.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Quality Control Sample (QC): a sample used to assess the performance of all or a portion of the measurement system.

Reporting Limit (RL, MRL): the level to which data is reported for a specific test method and/or sample.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

Surrogate: a substance with properties that mimic the analyte of interest but that are unlikely to be found in environmental samples.

System Performance Check Compounds (SPCCs): Selective analytes from the compound list that are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system.

Appendix B: Standard Preparation Tables

The standard formulations contained in this Appendix are recommended and are subject to change. If the concentration of the stock standard is different than those noted in this table, adjust the standard preparation formulation accordingly. Unless otherwise specified, prepare the standard solutions in methylene chloride using Class A volumetric glassware and Hamilton syringes. Unless otherwise specified for a standard solution, assign an expiration date of 6 months from date of preparation unless the parent standard expires sooner in which case use the earliest expiration date. See laboratory SOP BR-QA-002 *Standard Preparation* for further guidance.

The components and initial concentrations of the components that comprise the stock standard solutions purchased from commercial vendors are recorded in the in the reagent module of the laboratory's LIMS along with the final concentration of the prepared standard.

Internal Standard Solution

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Conc. (ug/mL)
Tetrahydrofuran-d8	Absolute (72261)	1000	50	4.0	12.5

4-Bromofluorobenzene (BFB) Stock Solution

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Concentration (ug/mL)
4-Bromofluorobenzene	Restek (30003)	5000	125	25	25

BFB Working Solution

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Concentration (ug/mL)
4-Bromofluorobenzene Stock	TAVTB	25	320	4.0	2.0

Calibration Intermediate Solution

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Concentration (ug/mL)
1,4-Dioxane	Restek (30287)	2000	10	2.5	8.0
1,4-Dioxane-d8	Absolute (30614)	2000	10		

Calibration Solution - High

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Calibration Stock	TAVTB	8.0	200	4.0	0.4

Calibration Solution - Low

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Calibration Stock	TAVTB	8.0	20	4.0	0.04

ICV Solution

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Concentration (ug/mL)
1,4-Dioxane	Ultra Scientific (NV-150-1)	100	8.0	4.0	0.2

Routine Working Calibration Standard Preparation

Sample Type	Final Conc. (ng/uL)	Low Calibration Solution (uL)	High Calibration Solution (uL)	ISTD (uL)	MeCl2 (uL)	Final Volume (uL)
CAL Level 1	0.002	5	0	4	95	104
CAL Level 2	0.020	50	0	4	50	104
CAL Level 3	0.100	0	25	4	75	104
CAL Level 4	0.200	0	50	4	50	104
CAL Level 5	0.400	0	100	4	0	104

Working ICV Standard Preparation

Sample Type	Final Conc. (ng/uL)	ICV Solution (uL)	ISTD (uL)	MeCl2 (uL)	Final Volume (uL)
ICV	0.200	100	4.0	0	104

EXTRACTION STANDARDS

The following standards are used to spike field and QC samples prior to extraction. Assign an expiration date of 6 months from date prepared unless the stock standard expires sooner in which case use the earliest expiration date. Store the prepared solutions under refrigeration and protected from light at a temperature of 4°C (±2).

LCS/Matrix Spike

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Concentration (ug/mL)
1,4-Dioxane	Restek (30287)	2000	100	100	2

Solvent: Methanol

Surrogate Spike

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Concentration (ug/mL)
1,4-Dioxane-d8	Restek (30614)	2000	10	10	2

Solvent: Methanol

Appendix C: Equations

Response Factor (RFx)

$$\text{Response Factor (RFx)} = \frac{\text{Area}_x \times \text{Concentration}_{is}}{\text{Area}_{is} \times \text{Concentration}_x}$$

Where:
x = compound,
is = Internal Standard

Relative Retention Time (RRT)

$$\text{Relative Retention Time (RRT)} = \frac{\text{Retention Time}_x}{\text{Retention Time}_{is}}$$

Where:
x = compound
is = Internal Standard

Mean Response Factor ($\overline{RF}$)

$$\text{Mean Response Factor } (\overline{RF}) = \frac{\sum_{i=1}^{n} RF_i}{n}$$

Where:
n = number of calibration levels

Standard Deviation of the Response Factor (SD)

$$\text{Standard Deviation of the Response Factor (SD)} = \sqrt{\frac{\sum_{i=1}^{n} (RF_i - \overline{RF})2}{n-1}}$$

Where:
n = number of calibration levels

Percent Relative Standard Deviation (RSD) of the Response

$$\text{Percent Relative Standard Deviation (RSD) of the Response} = \frac{SD}{\overline{RF}} \times 100\%$$

Percent Difference (%D)

$$\text{Percent Difference (\%D)} = \frac{RF_v - \overline{RF}}{\overline{RF}} \times 100\%$$

Where:
RF_v = Response Factor from the Continuing Calibration Verification (CCV)

Percent Drift

$$\text{Percent Drift} = \frac{\text{Calculated Concentration - Theoretical Concentration}}{\text{Theoretical Concentration}} \times 100\%$$

Percent Recovery (%R)

$$\text{Percent Recovery (\%R)} = \frac{C_s}{C_n} \times 100\%$$

Where:
C_s = Concentration of the Spiked Field or QC Sample
C_n = Nominal Concentration of Spike Added

Percent Recovery (%R) for MS/MSD

$$\text{Percent Recovery (\%R) for MS/MSD} = \frac{C_s - C_u}{C_n} \times 100\%$$

Where:
C_s = Concentration of the Spiked Sample
C_u = Concentration of the Unspiked Sample
C_n = Nominal Concentration of Spike Added

Relative Percent Difference (%RPD)

$$\text{Relative Percent Difference (\%RPD)} = \frac{C_1 - C_2}{\left(\frac{C_1 + C_2}{2}\right)} \times 100\%$$

Where:
C_1 = Measured Concentration of First Sample
C_2 = Measured Concentration of Second Sample

Sample Concentration (for average RF quantification)

Aqueous Samples

$$C_x = \frac{A_x \times C_{is} \times V_t}{A_{IS} \times \text{MeanRF} \times V_o \times V_i} \times DF$$

Where:
C_x = Concentration of compound (ug/L)
A_x = Area of quantitation ion
C_{IS} = Concentration of associated internal standard (ng)
V_t = Extract Volume (uL)
A_{IS} = Area of quantitation ion for associated internal standard.
Mean RF = Mean Response Factor from initial calibration, or 1 for a TIC or Alkane

V_o = Sample volume (mL)
V_i = Volume injected (uL)
DF = Dilution Factor

Solid Samples

$$C_x = \frac{A_x \times C_{IS} \times V_t \times GPC \times 10^3 g/Kg}{A_{IS} \times MeanRF \times W_s \times S \times V_i \times 10^3 ng/ug} \times DF$$

Where:
C_x = Concentration of compound (ug/L)
A_x = Area of quantitation ion
C_{IS} = Concentration of associated internal standard (ng)
V_t = Extract Volume (uL)
AIS = Area of quantitation ion for associated internal standard.
Mean RF = Mean Response Factor from initial calibration, or 1 for a TIC or Alkane
Ws = Sample weight (g)
S = Percent Solid
Vi = Volume injected (uL)
DF = Dilution Factor